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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

*THE CHANGEABLE HYDROLYTIC EQUILIBRIUM OF
DISSOLVED CHROMIC SULPHATE.*

BY THEODORE WILLIAM RICHARDS AND FREDERIC BONNET, JR.



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INTRODUCTION.

MANY eminent chemists have attempted to solve definitely the riddle involved in the dual nature of chromium solutions; but some doubt still remains concerning the precise interpretation of the facts. A complete review of earlier work would require far too much space at present; instead of such a review, there is given at the end of this paper a chronological bibliography of the subject, which will be referred to throughout the discussion by simply naming the appropriate date. The most satisfactory interpretation, based chiefly upon the work of Krüger (1844), Siewert (1863), Recoura (1887, 1890, 1895, 1899), Doyer van Cleef (1881), and Whitney (1896, 1899), seems to point to the following situation. The violet solution may be inferred to contain the chromic salt in a state comparable to that of other normal salts, while the green solution modified by heating appears to be hydrolyzed into acid and basic substances.† The hydrolysis seems in many cases to proceed to such an extent that about a gram atom of ionized hydrogen is developed for every two of chromium present, but the results are too conflicting to prove whether this is the indication of a nearly completed reaction or merely

* A part of this paper formed a portion of a thesis presented by F. Bonnet, Jr., for the degree of Ph.D. at Harvard University.

† Recoura has pointed out sharply the difference between the solutions thus modified and those obtained from salts which have been heated in the dry state. He names the two respectively "modified" and "green" chromic salts. The present paper has to do only with the former.

an accidental coincidence caused by an equilibrium which happens to yield an approximately commensurate mixture.

The present investigation was begun with the hope of discovering more about the nature of the complex substances produced, and thus explaining the mechanism of the change. The mode of attack consisted, first, in the more persistent and thorough application of the devices of others, and secondly of the introduction of other methods not used before on this problem. Among the former dialysis, migration experiments, electrical conductivity, and the distribution between two liquids were applied; among the latter, solid solution, catalytic sugar inversion, and the depression of the freezing point. While not a final unravelling of the tangle, the research has succeeded in narrowing the possibilities of interpretation.

THE PREPARATION OF CHROMIC SULPHATE.

The first problem to be solved was the preparation of chromic sulphate in a pure state on a scale large enough to supply plenty of material for the research. The sulphate was chosen for the research because when once converted into the green mixture, it regains its violet condition far more slowly than almost any other salt. Thus more time is available in which to study the green solution. This very fact, however, introduces a serious difficulty into the original preparation of the violet material, which is much hydrolyzed by a very moderate rise in temperature.

After sundry preliminary experiments which need not be recounted, it was found most convenient to prepare the violet salt according to the method of Traube (1848) with the additional precaution of careful cooling. When alcohol is run into a diluted mixture of sulphuric and chromic acids much heat is evolved, and the violet salt is accordingly hydrolyzed. By immersing the vessel containing the reacting solution in a freezing mixture and by adding the alcohol very slowly with continued agitation, the temperature may be kept below 10° , and less green chromic sulphate is formed. Upon adding subsequently an excess of alcohol the violet salt is precipitated in beautiful pale violet pearly flakes, which may be further purified by solution in water and reprecipitation by alcohol. We used an initial solution of chromic and sulphuric acids containing about 200 grams and 300 grams respectively of these substances dissolved in 600 grams of water. The yield of crystallized salt was about twenty per cent of the theoretical yield.

The salt thus obtained was analyzed for chromium by ignition and for sulphuric acid by precipitation, taking care to use conditions which

prevent the occlusion of chromium in the baric sulphate.* For every double gram atom of chromium there were found in two analyses 2.98 and 2.99 gram molecules of the sulphuric group, showing that the salt was normal. It was found by difference to contain 42.81 per cent or 16.3 molecules of water.

DIALYSIS.

Van Cleef in 1881 used dialysis as a means of partially separating the acid and the basic substances, and his method seemed worthy of a further trial. Accordingly we made a number of experiments in this direction. To our disappointment we found the results difficult to interpret quantitatively, partly because dialysis is a slow process, and during its dilatory progress the green solution has time to revert partially into the violet one. The experiments are, however, worthy of brief chronicling, because their qualitative interpretation is clear.

In the first place violet solutions were subjected to dialysis at temperatures from 16° to 20°, the results showing that the diffusing solution is essentially like that which remains behind. Parchment paper, carefully tied and with all accidental apertures sealed with collodion, was used as the diaphragm; and the level of the liquids was always adjusted in such a way as to prevent filtration.

For analysis, two precisely similar portions of a given solution were measured by means of a pipette. One of these portions was evaporated and ignited in a platinum crucible, and the other was diluted, and treated with slight excesses of ammoniac hydroxide, baric chloride, and hydrochloric acid in succession. The mixture was heated after the addition of the ammonia, and was digested for some time on the steam bath before filtration. This method, an application of that devised by Küster and Thiel † for exclusion of iron from baric sulphate, is successfully applicable to the case of chromium also. Here are the results: —

* A gram of the salt yielded in one case 0.2226, and in another 0.2229 grams of chromic oxide; again in one case 1.017 and in another 1.021 grams of baric sulphate. The baric sulphate was precipitated from a very dilute cold solution containing hydrochloric acid. The mixture was subsequently heated before filtration. The baric sulphate formed in this way is colorless and contains only traces of chromium. This matter will be discussed at length in another paper.

† *Zeit. anorg. Chem.*, **19**, 97 (1899). This matter will be discussed in detail in another paper.

DIALYSIS OF THE VIOLET SOLUTION.

No. of Exp.	Solution Analyzed.	Cr_2O_3 .	BaSO_4 .	Average Atomic Ratio $\text{Cr} : \text{SO}_4$.
1	Dialyte	0.0455	0.2066	2 : 2.95
2		0.0450	0.2043	
3		0.0508	0.2276	
4		0.0504	0.2285	
5	Residue	0.1120	0.5180	2 : 2.99
6		0.1119	0.5118	
7		0.1713	0.7847	
8		0.1717	0.7815	

Thus the "dialyte," or the portion which passed through the diaphragm, seemed to be slightly more basic than that which remained behind — but the difference is scarcely greater than the possible errors of analysis. The diffusion is obviously concerned chiefly with the normal salt, $\text{Cr}_2(\text{SO}_4)_3$.

Very different results were obtained when the green solution was subjected to dialysis. Below are given the corresponding analyses of material which had been hydrolyzed by heating to the boiling point : —

DIALYSIS OF THE GREEN SOLUTION.

No. of Exp.	Solution Analyzed.	Cr_2O_3 .	BaSO_4 .	Average Atomic Ratio $\text{Cr} : \text{SO}_4$.
9	Dialyte	0.0470	0.2951	2 : 4.09
10		0.0471	0.2947	
11	Residue	0.1174	0.5071	2 : 2.82
12		0.1172	0.5062	

Here the difference between the analyses of the "dialyte" and residue is vastly greater than any possible analytical error, and in the opposite direction from the slight one observed in the case of the violet salt. The portion which diffused through the diaphragm contained much more of the sulphuric group in proportion than that which remained behind. From the analysis, the deficiency of acid in the residue seems to be less than the excess of acid in the dialyte merely because less than quarter of the material was allowed to pass through the diaphragm. The total deficiency, on the one hand, of course exactly equalled the total excess on the other. These facts agree essentially with the results of van Cleef.

In support of these data it is worthy of note that the green boiled solution is strongly acid to methyl orange.

Clearly the results of dialysis, complicated as they are by the continual reversion of green to violet, are too involved to furnish more than qualitative evidence that hydrolysis has really taken place in the green solution. The qualitative evidence is nevertheless indubitable.

CATALYTIC ACTION.

Long suggested in 1897 that the green chromium solution probably inverts cane sugar, while the violet does not. Modern hypothesis contends, as is well known, that ionized hydrogen is the cause of this kind of catalytic action; hence the speed of the inversion might afford a measure of the extent to which the chromic solution has been hydrolyzed.

The strength of color of the solutions makes the use of the polarimeter impossible, hence the ingenious method used by Kahlenberg and Davis* was employed for determining the extent of the inversion. This method depends upon the fact that invert sugar has about twice as great a depressing effect on the freezing point of water as the cane sugar from which it is made. The catalyzer is assumed to exert a constant effect on the freezing point. Thus the progress of the inversion may be followed by taking successive measurements of the freezing point of the solution.

Our sugar solution contained about 250 grams in the litre. It was carefully sterilized by intermittent heating on three successive days; and the permanent apparatus for delivering measured quantities of the solution was also sterilized. If suitable precautions of this kind are taken, the solution will of course preserve its strength for months. A

* Jour. Am. Chem. Soc., 21, p. 1 (1899).

fourth-molar solution of crystallized chromic sulphate (170 grams in a litre) was made; and a portion of this was boiled in a Jena flask with a reflux condenser and rapidly cooled. Thus were obtained a violet and a green solution containing the same concentration of chromium, the latter being always used very promptly after its preparation in order to forestall as much as possible the reversion to the violet condition.

The freezing point determinations were made in large test-tubes in a Beckmann apparatus. Each tube contained 20.00 cubic centimeters of the sugar solution, and 5.00 cubic centimeters of the chromic solution or of another solution whose catalytic action was to be tested. In order to determine the freezing point of the cane sugar solution another tube-ful was prepared in which these last 5.00 cubic centimeters were of pure water.

The freezing points of these solutions were determined in the first place immediately after mixing. They were then placed in a water tank of fairly constant temperature (not far from 17°); and from time to time further determinations of the freezing point were made.

Oddly enough the green and violet solutions caused in the first place the same depression of the freezing point of the sugar solution. It is not wholly safe to conclude from this, however, that the average number of molecules in a given bulk of the two solutions would be identical if the sugar were absent; for it is not impossible that a portion of the complex substances existing in the green solution may combine with sucrose, as we later found them to affect gelatine.

In a short time the catalytic action of the two solutions was seen to be very different. The green solution inverted the sugar rapidly, while the violet solution had only a slight action. This is indicated by the following table of data and results, most of which explains itself. The sixth column labelled "acid" represents the freezing points of a 0.468 normal solution of hydrochloric acid. Each of the temperatures represents an average of at least four readings of the thermometer. The changes in the zero point of the thermometer were registered by freezing-point determinations of pure water; these were essentially parallel with the changes in the pure sugar solution and are not recorded in the table on the opposite page.

It is evident from this table that the green solution possessed at least twelve times as great a catalyzing power as the violet, while the acid catalyzed at first about 3.5 times as fast as the green. As the sucrose diminishes in concentration the speed of the reaction diminishes from this cause, and as time goes on, the green slowly reverts to the violet,

PRELIMINARY SERIES OF CATALYTIC EXPERIMENTS.

Fresh Violet and Boiled Green Solution at $17^{\circ}\pm$.

Time.	Data: Observed Freezing Points.				Results: Lowering of Freezing Point with Time.		
Hours.	Sugar.	Violet.	Green.	Acid.	Violet.	Green.	Acid.
..	4.060	3.760	3.760	3.655
18	4.071	...	3.672	3.326	...	0.099	0.340
46	4.086	3.770	3.617	3.127	0.016	0.169	0.464
68	4.086	3.765	3.537	3.007	0.021	0.249	0.674
138	4.071	3.735	3.339	2.690	0.036	0.432	0.976

hence the first few hours of the experiment give the best clue to the composition of the solution.

The inference to be drawn from this result is, then, that the fourth molar green solution contains about as much ironized hydrogen as a $\frac{0.468}{3.5} = 0.133$ normal solution of hydrochloric acid, or every ion of

hydrogen corresponds to 3.7 atoms of chromium. This is a much smaller proportion of ionized hydrogen than that found by Recoura and Whitney (1:2); but it must be remembered that both of these experimenters made their determinations by neutralization, a proceeding which might well displace an existing equilibrium and make the amount of ionized hydrogen seem too large.

In another series of experiments the conditions were varied. The chromic solution was hydrolyzed for many hours at 50° , instead of by boiling. A temperature of 30° was chosen for the inversion in order that its speed might be greater than before; this temperature was maintained by means of an Ostwald thermostat. The acid solution which served as a measure of the ionized hydrogen present was much diluted for this comparison, because it had been shown before to be stronger even than the acid in the chromic solution which had been boiled. By two or three preliminary tests it was found that an acid having about the same inverting power as the green solution prepared at 50° was very nearly tenth normal. Below are given the data and results of the series, arranged in the same way as before. The hydrochloric acid whose results are recorded in the fifth and last columns was 0.105 normal.

FURTHER CATALYTIC EXPERIMENTS.

Fresh Violet and Green Solutions at 30°.

Time.	Data : Observed Freezing Points.				Results : Lowering of Freezing Point with Time.		
Hours.	Sugar.	Violet.	Green.	Acid.	Violet.	Green.	Acid.
..	3.835	3.542	3.537	3.922
6	3.846	3.528	3.390	...	0.011	0.154	...
20	[3.835]	3.487	0.435
23	3.860	3.470	3.130	...	0.083	0.428	...
29	[3.850]	3.435	3.040	...	0.108	0.508	...
47	3.188*	2.640	2.133	...	0.236	0.748	...
53	[3.183]	2.593	2.010	...	0.283	0.871	...
68	[3.835]	3.032	0.890

These results contain much of interest ; their outcome is best seen in the accompanying diagram. (Dotted curves H, B, and A.) The typical logarithmic curve whose inclination depends solely upon a constant concentration of catalyzer and the changing concentration of the sucrose is shown by the line A, representing the performance of the acid recorded in the last column above. Any departure from this curve must indicate some other superposed reaction.

Neither of the curves of the chromium solutions (B and H) shows precise similarity to the typical curve, but that of the green solution (B) is of the same general character. Especially at first its irregularity is slight; here it acts as if the concentration of its ionized hydrogen were perhaps 0.095 normal.

On the other hand the curve of the violet solution (H) indicates clearly an important superposed reaction. At first, in confirmation of the previous results, it seems to contain about a tenth as much acid as the green salt ; but the rate of inversion steadily *increases* with time, instead of slightly decreasing. This anomaly is only to be explained by supposing the formation of more green substance and acid, — that is, by the hydrolysis of the violet salt at 30°. This conclusion was verified by the

* Thermometer reset.

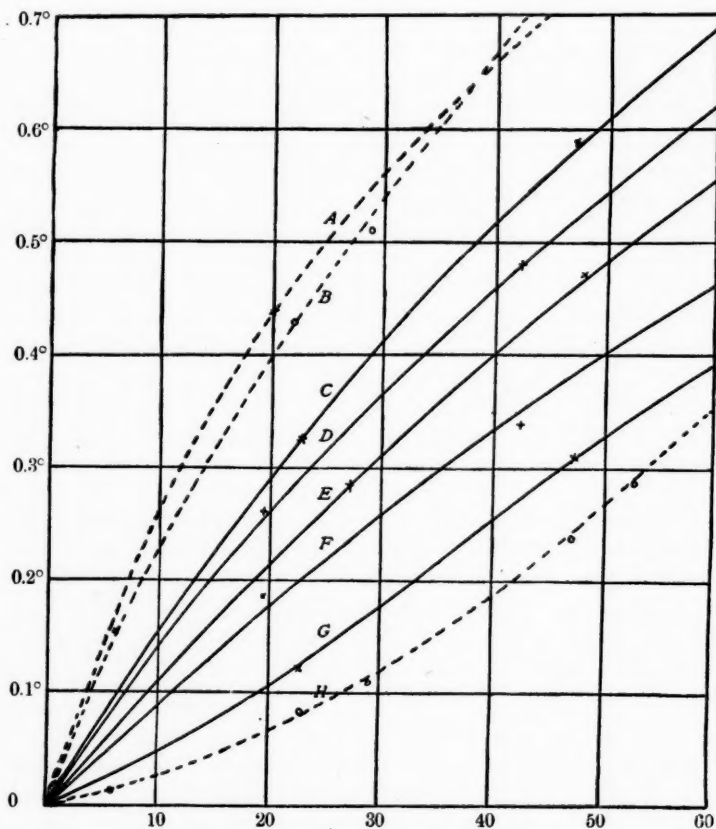


FIGURE 1. — THE RESULTS OF CATALYSIS.

Hours are plotted abscissally, and changes in the freezing point ordinately. The curve *A* corresponds to pure acid, *B* to freshly boiled green solution, *H* to freshly made violet solution, and *E* to both of these solutions after having been kept for a month at 30°.

color of the solution, which at the end of five days had become decidedly green.

This series of experiments thus showed the following facts:—

First, the green salt hydrolyzed at 50° contained slightly less acid than that hydrolyzed at 100°, the respective acidities being perhaps 0.10 and 0.13 normal in a $\frac{1}{4}$ molar solution.

Secondly, at 30° , in the presence of sucrose and glucose, the violet solution is converted at least in part into the green.

From these experiments it seemed probable, since the effect of the sugar could hardly be great, that the relation between the green and the violet solution is a changeable one, depending upon the temperature, and attaining at each temperature a definite equilibrium. It seemed highly desirable to test this conclusion by suitable experiments.

Accordingly a fourth-molar violet and a fourth-molar boiled green solution, both free from sugar, were placed in a thermostat at 30° . After five days, 5 c.c. of each solution was removed by means of a pipette, mixed with two portions of 20.00 c.c. each of a sugar solution, and followed by means of the freezing point. Unfortunately the supply tube containing the green solution was then broken, so that a new one was placed in the thermostat. At the end of twelve days for the violet and seven days for the new green solution, new portions were mixed with sugar; again eight days afterward this process was repeated, and yet again after nine days more. There are given below the figures of the first two and the last two of these freezing point determinations; the others confirm the verdict of these and are omitted to economize space. For the same reason only the additional depressions of the freezing point are given;—these were found in the manner already described. The results are plotted on the diagram (curves C, D, E, F, G), which gives also in dotted lines those of the previous series.

EQUILIBRIUM OF GREEN AND VIOLET SOLUTIONS.

Depression of Freezing Points of Solutions Maintained at 30° .

Time of Inversion.	G. Violet Hydro-lyzed 5 Days at 30° .	C. Green Dehydro-lyzed 5 Days at 30° .	Time of Inversion.	F. Violet Hydro-lyzed 12 Days at 30° .	D. Green Dehydro-lyzed 7 Days at 30° .	Time of Inversion.	Violet Hydro-lyzed 20 Days at 30° .	Green Dehydro-lyzed 15 Days at 30° .
22.7	0.120	0.323	19.5	0.190	0.263	19	0.205	0.213
47.2	0.302	0.587	42.5	0.338	0.473	66	0.473	0.538
70.7	0.433	0.768	66.5	0.497	0.672	E.	29 Days.	24 Days.
94.7	0.550	0.880	91	0.635	0.817	27.2	0.285	0.286
165	0.827	1.100	116.7	0.720	0.900	48	0.470	0.468
184	0.877	1.120	186.7	0.900	1.030	96	0.735	0.740
207	0.923	1.140	212	0.937	1.060	150	0.900	0.890

Thus in about a month the violet and green solutions, kept in a thermostat at 30° , had become identical in their inverting power and probably in every other respect. (Curve F.) The concentration of acid corresponding to this equilibrium is not far from 0.043 normal, judging from the inclinations of the curves at the origin.

Thus the conclusion which prompted the last experiments is satisfactorily confirmed. Evidently the hydrolytic equilibrium between the green and the violet salts varies continuously with the temperature. At 18° , in a fourth-molar solution of salt, the violet salt is chiefly in evidence, the inverting power corresponding to only a small fraction of the green solution. At this temperature even the slight hydrolysis which occurs must take place very slowly, and months would be needed to reach the true equilibrium. This conclusion is in accord with the spectroscopic results of Erhard (1875) and Vogel (1878), and explains the fact noted by Lecoq de Boisbaudran (1874) that a violet chromic solution increases slightly in volume during long standing at 20° . At 30° the acid resulting from the hydrolysis attains in equilibrium a concentration of about 0.04 normal; at 50° of about 0.10 normal, and at 100° of at least 0.13 normal. The last two figures are probably too low because the green solution must obviously begin to "dehydrolyze" as soon as it cools.

In the light of these facts it is clearly impossible from any direct analysis of the solution to determine the composition of the compounds resulting from the hydrolysis. Evidently, too, the process of neutralization by alkali adopted by several experimenters will tend to hasten the incomplete hydrolysis by removing the ionized hydrogen; but at the ordinary room temperature it is unlikely that any definite equilibrium will be reached in a short time. Hence the composition assigned to the basic compound by Recoura and Whitney is by no means certain; it might have been varied by time and by change of temperature. This indeed is indicated by the disagreeing formula of Siewert.

It seemed possible, however, that if the acid were in any manner removed, without introducing any other substance, the basic substance might finally attain a definite composition. Two methods suggested themselves for this purpose; first, the repeated "shaking out" of the acid by another solvent, after repeated warming; and secondly, the long continued agitation of the green solution with chromic hydroxide. Descriptions of experiments of these kinds are recorded below.

THE EXTRACTION OF THE GREEN SOLUTION WITH
ALCOHOL AND ETHER.

No. of times boiled and extracted.	Weight of Cr_2O_3 .	Weight of BaSO_4 .	Atomic Ratio $\text{Cr}_2 : (\text{SO}_4)_x$. $x =$
1	$\left\{ \begin{array}{l} 0.1408 \\ 0.1407 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.5448 \\ 0.5435 \end{array} \right\}$	2.52
1	0.1034	0.4000	2.52
2	0.3981	1.4992	2.46
3	0.0724	0.2676	2.41
5	0.1571	0.1571	2.25
6	0.0474	0.1498	2.06
9	0.0669	0.1553	[1.52]
14	$\left\{ \begin{array}{l} 0.0322 \\ 0.0321 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.0978 \\ 0.0970 \end{array} \right\}$	1.98
12	$\left\{ \begin{array}{l} 0.0760 \\ 0.0760 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.2272 \\ 0.2261 \end{array} \right\}$	1.94

DISTRIBUTION BETWEEN TWO SOLVENTS.

In 1863 Siewert endeavoured to distinguish between the acid and basic salt by distributing the two substances between two solvents, in which it was reasonable to suppose that the two would have different solubilities. He treated an aqueous solution with a mixture of ether and alcohol for this purpose, and found that the viscous aqueous solution remaining was basic, containing only about 2.4 SO_4 instead of 3 SO_4 for each Cr_2 . In the light of the facts described above, it seemed to us possible that this basic substance was mixed with some unchanged chromic sulphate; because there is no proof that the hydrolysis was complete in the presence of the acid, and several reasons for believing that it was not complete. This inference could be tested by boiling the green viscous residue with water after its acid had been removed. If the compound had been hydrolyzed as much as possible, further extraction with alcohol and ether could have no further effect; but if the hydrolysis were incom-

plete, the second boiling would produce more acid capable of extraction with alcohol and ether.

In our experiments a platinum vessel was used for heating the liquid, and the process of boiling and extraction was repeated fourteen times on one sample and twelve times on another. From time to time portions of the green viscous substance were dissolved in water, and two equal portions of the solution were taken for analysis. The chromic oxide was found by evaporation and ignition, the sulphuric acid by precipitation with successive additions of ammonia, baric chloride, and hydrochloric acid in the manner already described. Thus the "atomic ratios" between chromium and sulphuric acid were found. Above are the data and results. The first and the last two analyses were made in duplicate; the others were each single comparisons.

Thus the solution became more and more basic as the treatment proceeded. After the eighth extraction a precipitate appeared on each boiling; this was not filtered off before the ninth analysis, but subsequently it was removed before each analysis. Before the twelfth boiling in each case a constant ratio was reached, which was not altered by further treatment. This corresponds closely to $\text{Cr}_2 : (\text{SO}_4)_2$; and at first it was supposed that the formula of the compound might be simply CrSO_4OH . In order to test this assumption, it was thought desirable to discover if the same equilibrium could be attained in another way, the second method mentioned at the end of the last section.

THE TREATMENT OF THE GREEN SOLUTION WITH CHROMIC HYDROXIDE.

In order to attain a maximum of dissolved chromic oxide, the pure green solution used above was digested on the steam bath in a platinum dish with pure chromic hydroxide for several hours. A portion was then rapidly filtered, and analyzed, while the remainder was heated for nine hours more. The analyses of the two samples are given on the next page.

The relation of the chromium to the sulphuric acid in this solution, which had evidently attained a constant composition, was thus found to be essentially like that obtained by extraction with alcohol and ether. The two comparable average results are respectively 1.97 and 1.96, agreeing essentially with the formula CrOHSO_4 .

Two circumstances imply that this is not the basic limit of chromic sulphate in cold solutions, however. One of these is the fact that upon extracting such a solution with ether, a clear solution was left which de-

MAXIMUM BASIC CONDITION OF HOT CHROMIC
SULPHATE SOLUTION.

Time of Digestion.	Weight of Cr_2O_3 .	Weight of BaSO_4 .	Atomic Ratio $\text{Cr}_2 : (\text{SO}_4)_x$ $x =$
4 hours	0.1081	0.3267	1.971
	0.1080	0.3260	
13 hours	0.0732	0.2205	1.968
	0.0733	0.2214	

posited chromic hydroxide on boiling; and the other is the fact that this boiled solution was found to be strongly acid to methyl orange.

Thus the solution boiled with chromic hydroxide must contain ionized hydrogen, and hence the basic substance present must be even more basic than CrOHSO_4 , the agreement with this formula being accidental.

In accordance with this inference, it was found that dilute caustic alkali could be added to the solution without producing a permanent precipitate. The same result — the removal of the ionized hydrogen — may be better accomplished by shaking the solution at ordinary temperatures with chromic hydroxide. Even the violet solution may be quickly converted into the green in this way, as Siewert has shown. The hydroxide was prepared by cold precipitation with a slight excess of ammonia, and was washed until free from sulphuric acid. The violet solution was treated with an excess of this precipitate, and the mixture was shaken in a tightly stoppered bottle in an automatic shaking machine for several days, portions being removed from time to time for analysis. Opposite are given the results of this work. The solution was fourth-molar and the temperature about 20° .

The constant results indicate saturation. Thus a decrease in acid from 1.97 to 1.59 — or perhaps better an increase in base from 2.00 to 2.48 — occurs on cooling in the presence of excess of hydroxide. This ratio corresponds almost exactly to $\text{Cr}_6 : (\text{SO}_4)_4$, a relation which demands the complex formula $\text{Cr}_6(\text{SO}_4)_4(\text{OH})_7$. The possibility still existed that some ionized hydrogen was present even at 20° , because so much more ionized hydrogen was needed at 100° in order to preserve the equilibrium.

In order to test this point the rate of inversion of sugar at 30° by this

MAXIMUM BASIC CONDITION OF COLD CHROMIC
SULPHATE SOLUTIONS.

Time of Shaking.	Weight of Cr_2O_3 .	Weight of BaSO_4 .	Atomic Ratio $\text{Cr}_2 : (\text{SO}_4)_x$ $x =$
2 days	0.1299	0.3162	1.588
3 days	0.1128	0.2757	1.593
	0.1127	0.2750	
4 days	0.1120	0.2740	1.595
	0.1120	0.2736	

saturated green solution was tested; and it was found that in thirty-six hours the additional depression of the freezing point of sugar was 0.017° , while in eight days it was 0.125° . This rate of reaction corresponds to a concentration of acid of only about $\frac{1}{400}$ normal, even supposing that the basic salt itself has no catalytic effect. Conclusions drawn from such an observation must of necessity be doubtful.

It seems probable, nevertheless, that there may exist in solution a chromium salt at least as basic as 5 : 4—a substance far more basic than that found by Recoura and Whitney, whose ratio was 5 : 6.25. This probability of course by no means proves that there are not several stages of hydrolysis, each product being indistinguishably green. Moreover, the equilibrium in a solution at one concentration may be displaced at another. These considerations disclose an almost endless opportunity for investigation. Since, however, the time at our disposal was not unlimited, another direction was now pursued, in the hope that it might lead more directly to the desired goal.

THE OCCLUSION OF CHROMIC SALTS IN BARIC SULPHATE.

It is well known that iron is carried down with baric sulphate, when the iron is present in the ferric condition. This circumstance has formed the subject of numerous investigations.* In a recent paper,† it has been

* Among the most important of these are Jannasch and Richards, Jour. prakt. Chem. [2], **39**, 321 (1889); Schneider, Zeit. phys. Chem., **10**, 425 (1892); Küster and Thiel, Zeit. anorg. Chem., **19** (1899).

† Richards, Proc. Am. Acad., **35**, 377 (1900); Zeit. anorg. Chem., **23**, 383 (1900).

pointed out that this *occlusion* is probably due to the distribution of a definite molecular species between the solvent and the precipitate at the moment of formation of the latter. Various data concerning different precipitates seem to support this conclusion so strongly that it may be used as a working hypothesis.*

Thus the composition of the occluded matter may afford a clue as to the nature of some of the molecular species present in the solution. The only difficulty in the interpretation of the results is due to the possibility that more than one molecular species may thus distribute itself between the solution and the precipitate.

In the cases cited above, which furnished the basis for these conclusions, it was shown † that as a rule electrically neutral substances rather than ionized ones seemed to be thus distributed. This is indeed a reasonable conclusion; for the ionizing power of cool solids such as baric sulphate is probably much less than that of water.

In view of these inferences, it seemed possible that the careful analysis of baric sulphate precipitated in the presence of much green chromic salt might furnish valuable evidence as to the nature of the complex substances present. Accordingly precipitates were made under varying circumstances, and analyzed with great care. The first experiments showed that green chromic salt is occluded by baric sulphate to an extent fully as great as ferric iron, while the violet salt is scarcely occluded at all. Since the baric sulphate, after all the sulphuric acid had been precipitated from the solution, weighed less than the amount corresponding to the sulphuric acid known to be present, it was clear that the chromium must be present in the precipitate as sulphate. The case seemed, in short, to be precisely similar to that of iron, carefully studied by Jannasch and Richards in the paper already cited.

Our present object was to carry further the method of study followed in that paper, and to determine more precisely the nature of the occluded compound. A first step in this direction was to discover whether or not green chromic chloride might be occluded as well as sulphate; for the occlusion of chromic chloride would seriously interfere with the possibility of satisfactory interpretation.

For this purpose it was not enough to determine the chlorine in the precipitated baric sulphate, since baric chloride is known to be occluded

* See for example Richards, McCaffrey, and Bisbee, These Proceedings, 36, 377 (1901).

† Richards, *loc cit.*

by this salt.† It seemed possible, however, that since the complex green sulphate is so tardy in the attainment of its equilibrium (a fact indicated by the preceding work), it might also not form at once from the complex green chloride. In this case it might be possible to precipitate baric sulphate from a solution of chromic chloride before the green sulphate had been allowed time to form.

The answering of this question was experimentally easy. Pure solutions of sodic sulphate, chromic chloride, and baric chloride were prepared of convenient concentrations, which corresponded to 1.558 gram of baric sulphate from the volumes used.

In a first experiment, the chromic chloride and sodic sulphate were heated separately to the boiling point, quickly and thoroughly mixed, and at once precipitated by baric chloride. After the precipitation the mixture was diluted four-fold from its small initial volume to about two-tenths of a litre, and was digested for several hours on the steam bath in order to facilitate filtering. The precipitate was weighed and its percentage of chromium found by fusion with alkaline carbonate and nitrate, reduction with alcohol, and precipitation with ammonia.

In this way, the baric sulphate was found to weigh 1.562 gram and to contain 0.0100 gram of chromic oxide. An experiment similar in every way, except that an hour elapsed between the mixing of chromic chloride with sodic sulphate and the precipitation, yielded only 1.472 grams of precipitate, containing 0.0582 gram of chromic oxide. Evidently far more chromic salt was occluded when time for the formation of the complex sulphate was allowed.

As would be expected, this difference became still more evident when the mixture and precipitation was carried on at 20°. A precipitate which had been formed as soon as possible after the mixing of the chromic and sulphate solutions appeared perfectly white, and contained only 5.5 milligram of chromic oxide; while fifteen minutes, an hour, and three hours' delay in precipitation led to greener and greener precipitates containing respectively 9.4, 13.6, and 14.7 milligrams of chromic oxide respectively.

These experiments were all verified by repetition, so that the following conclusions seem to be indubitable:—

(1) The chief occluded body is neither the simple chromic ion nor a complex chloride, but rather a sulphate.

† Richards and Parker, *These Proceedings*, **31**, 67 (1894); *Zeit. anorg. Chem.*, **8**, 413 (1895).

(2) That time is required for the formation of this complex sulphate, especially at low temperatures.

These reasonable conclusions are entirely in accord with the outcome of our previous work. It became now possible to determine by analysis the basic nature of the occluded body.

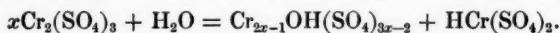
In order to attain this end, the occlusion was made as marked as possible by allowing plenty of time for the formation of the complex sulphate. Four portions of several grams each of baric sulphate thus badly contaminated with chromium were precipitated from a solution, which had been made strongly acid with hydrochloric acid in order to prevent excessive hydrolysis. Each portion of precipitate was analyzed twice, making eight analyses in all. Every analysis indicated a deficiency of sulphuric acid in proportion to barium and chromium (a deficiency at least as great as that demanded by Recoura's formula), although the extent of the deficiency was not exactly the same in every case. The variations are inessential, and the average result will serve for the present purpose. The precipitate was found to contain 57.24 per cent of barium, 0.39 per cent of chromium, and 40.84 per cent of the sulphuric radical. This quantity of barium should correspond to 40.01 per cent of the sulphuric radical; an amount which leaves 0.83 per cent to be associated with the chromium. This is a considerable deficiency, since 0.39 parts of chromium corresponds to 1.16 parts of the sulphuric radical in the normal sulphates.

Yet a greater amount of occlusion might obviously be obtained by causing the formation of more of the complex sulphate by neutralization of the acid before precipitation, but such a basic solution cannot be heated without the obvious deposition of chromic hydroxide, as has been already stated. Hence experiments were made with a cold green solution, saturated with chromic hydroxide. From the clear solution baric sulphate was precipitated, and allowed to stand for a long time. The baric sulphate thus formed was washed with cold water to prevent the accidental hydrolysis of the adhering filtrate. In four successive analyses of two separate specimens of gently dried baric sulphate thus made, the following percentages were found: barium, 55.46, 55.50; 55.14, 55.29; chromium, 0.64, 0.64; 0.65, 0.80; sulphuric radical, 39.67, 40.07; 39.53, 39.50. The averages of all these values are 55.35, 0.68, and 39.69. This quantity of barium corresponds to exactly one per cent less of sulphuric acid than the figure actually found, hence this 1.00 part may be supposed to be associated with 0.68 part of chromium. But this quantity of chromium should be associated with nearly twice as much sulphuric acid

(1.88 parts) if the salt were normal. The discrepancy indicated only 1.6 atoms of the sulphur for every 2 atoms of chromium, a proportion as nearly as possible identical with that obtained by the analysis of the pure ultra-basic solution.

Any conclusions based upon these figures must be somewhat insecure, because the data are only the somewhat variable differences between large quantities, and because traces of other groups besides the complex sulphate are probably occluded by the basic sulphate. Nevertheless it seems safe to say that the chief occluded body causing the green color of the impure precipitate is basic, and that nearly half of the sulphuric acid which should be combined with the chromium may be replaced by hydroxyl. There is nothing in the results to prove that there are not several soluble green basic salts, of different degrees of hydrolytic decomposition; but even the least basic of these, obtained in a strongly acid solution, seems to be more basic than that represented by the formula of Recoura.

Having thus determined in various ways the existence of a basic complex, it seems highly desirable to discover whether or not an acid complex containing chromium also exists, according to the possible equation,



This matter forms the subject of the following section.

MIGRATION EXPERIMENTS.

Whitney showed in 1899 that the method of Lodge* for observing electrolytic migration afforded proof of the presence of ionized hydrogen in the green solution. We were desirous to carry this matter further, in order to discover whether or not there was any observable migration of a green complex anion, concerning whose possible existence Whitney was not anxious. In a number of experiments according to Lodge's method we obtained inconclusive results, which were found to be due to the fact that the green solution coagulates the gelatine and leaves free passages for convection in the expelled solution. Gelatine thus coagulated by the green chromium solution cannot be melted by warming, hence it is evident that a compound must be formed. On this account we rejected gelatine, and continued the migration experiments with the help of an apparatus similar to Hittorf's.

The diagram illustrates this arrangement. The glass cups or cells

* O. Lodge, B. A. Reports, 305 (1886). See also Whetham, Phil. Mag. [5], 38, 392 (1894); Orme Masson, Zeit. phys. Chem., 29, 501 (1899).

were provided below with carefully tied diaphragms of parchment paper made tight at the sides with collodion. The middle cup contained a green chromium solution which had been freed from acid by shaking with chromic hydroxide, while the others contained cadmic sulphate. Cadmium electrodes were used to prevent the formation of ionized hydrogen or hydroxyl.

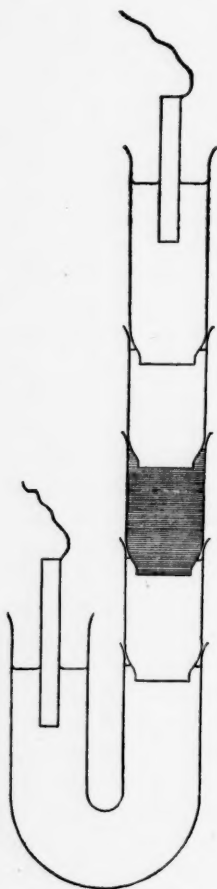


FIGURE 2.

Because gravity caused a slight filtration, only the presence of chromium in the cup above the green solution could be taken as evidence of certain electrolytic migration. Hence the positive current was run first downwards in order to determine if there was any anodic migration of chromium, and then in subsequent experiments upwards in order to determine if there was any cathodic migration. In order to determine the chromium, the cadmium in the cell was first removed as sulphide. No trace of chromium was found in the anode solution after 340 coulombs of electricity had been passed through the apparatus, as indicated by the deposition of 0.1119 gram of copper in a serially connected coulometer.

On the other hand, in an experiment in which the cathodic migration was tested, 183 coulombs carried 36.6 mg. of chromium, corresponding to 19.3 grams of chromium for each Faraday's equivalent of 96,580 coulombs.* The cation was green. The quantitative result is surprisingly large. Since the atomic weight of chromium is only 52, it is clear that each atom of chromium cannot be associated with over two charges, and probably with not more than a single charge. Assuming from the absence of chromium in the anodic fluid that the sulphuric ion alone migrates in that direction, and that the mobility of this anion is 70,† the mobility of the chromium group must be 41 on the assumption that each chromium has a single charge and 243 on the assumption that each has a double

* The weights of chromic oxide found were 53.5 and 48.2 mg. respectively.

† Kohlrausch and Holborn, *Leitvermögen der Electrolyte*, p. 200.

charge. The latter of these figures is improbably large, while the former is plausible, approximating the values for zinc and magnesium. Hence it seems probable that the number of charges does not greatly exceed the number of atoms of chromium. It is not impossible that the cation is CrO^+ or $\text{Cr}(\text{OH})_2^+$, which has been shown by Siewert (1863) and Whitney (1896) to be the most probable cation of boiled chromic chloride and nitrate. On the other hand of course there is nothing to show that the ion is not a complex one, with a valence about equal to the number of chromium atoms, or at least a mixture of complexes with an average valence no greater than this. This conclusion would be consistent with that reached in other ways; for if not all the normal valence of chromium is available, it is obvious that some of it must be held by undissociable hydroxyl, or hydroxyl and sulphuric acid, in a basic complex.

The absence of chromium from the portion migrating towards the anode overthrows the hypothetical equation involving an ionized complex acid, which otherwise seemed plausible.*

MOLECULAR WEIGHTS.

The next step, suggested by the foregoing paragraph, is an investigation of the average molecular weights of the dissolved substances. In mixtures so complicated the interpretation cannot be certain, but may nevertheless afford some clue to the situation. It has already been pointed out that the depression of the freezing point is the same for a green solution hydrolyzed only by heating and a violet solution of equal concentration, when sugar is present, — namely about 0.30° with a twentieth molar solution. Since a molar solution should give a depression of 1.85° according to Raoult's law, there may be supposed to be
$$\frac{20 \times 0.30}{1.85} = 3.2$$
 active particles for each molecule of $\text{Cr}_2(\text{SO}_4)_3$ at this

dilution, or the average molecular weight is 122. As has been already suggested, this conclusion is somewhat in doubt, because of the presence of sugar, which may have an unknown specific action. Since much ionized hydrogen is formed during the hydrolysis, it is obvious that the remainder of chromium is probably condensed into a more complex compound when the hydrolysis takes place — otherwise the number of active particles would increase on hydrolysis instead of remaining constant. This interpretation is supported by the freezing points of the more basic

* Krüger (1888) and Siewert (1845); also Richards, *Zeit. anorg. Chem.*, **23**, 388.

solutions. When the solution is saturated at 100° with chromic hydroxide, a mixture containing the same amount of chromium per litre as before causes a depression of the freezing point of only 0.080° , and a parallel mixture saturated at 20° with chromic hydroxide causes a depression of only 0.071° , instead of 0.30° found at first.*

This decrease in the depression of the freezing point indicates a decrease in the number of dissolved particles, the final value corresponding to only 1.5 particles for every four chromium atoms. These results are only preliminary ones; they will be repeated and amplified in the near future. As far as they have any significance, they seem to indicate that one of the green bodies really possesses a high molecular weight, as Recoura and Whitney believed, although at least one of these bodies is more basic than these investigators assumed.

CHEMICAL RETARDATION OF THE HYDROLYSIS.

The preceding experimentation is unanimous in indicating that at least one soluble green basic substance is found by the hydrolysis of violet chromic salts, and that the extent, and of course also the speed, of this hydrolysis is dependent upon the temperature.

If this is true, the neutralization of the acid formed by hydrolysis should greatly favor the formation of the basic substance, while on the other hand the addition of more acid should retard this formation. The former of these consequences has already been shown to hold true—it introduces an accidental circumstance into the work of both Whitney and Recoura. The latter of the consequences remains to be proved.

With this object freshly prepared solutions of the violet and merely boiled green solution, of one-fortieth molar strength, were each divided between four test-tubes, every tube containing ten cubic centimeters. To one test-tube of each color was added a gram of ammoniac chloride, to another of each color a gram of sodic sulphate, and to a third of each color a gram of sulphuric acid, while the fourth of each color was left unmixed. Each was slightly diluted until all were equal in volume. All were allowed to stand together in the laboratory at temperatures varying from 20° to 27° . At the end of a week the green and violet tubes were distinctly less different than at first, and in each series the test-tube containing excess of acid was unquestionably the most violet. The sodic sulphate seemed very slightly, and the ammoniac chloride somewhat more

* The actual depressions measured were respectively 0.053° and 0.108° for solutions yielding 0.0503 and 0.1156 Cr_2O_3 per 10 c.c. respectively.

prominently, to assist the hydrolytic effect, as judged by the greenness of the solutions — but these changes were subordinate in magnitude, and inessential.

Qualitative though they were, these experiments furnished final evidence that the effect is hydrolytic.

In this paper no attempt has been made to study the colloidal acid sulphates of Recoura and Whitney, made by heating the dry salts to a higher temperature. These introduce a new complication into the theoretical interpretation of the behavior of chromium; but they have been shown by Whitney to be unstable in solution, and hence probably do not enter into the equilibrium under consideration.

SUMMARY.

Our results, which amplify rather than contradict the best of the preceding work, may be summarized as follows: —

1. It is shown that the immediate yield of violet chromic sulphate from chromic anhydride is much increased if the reducing reaction is allowed to take place at low temperatures.

2. Violet chromic sulphate was found to dialyze in normal atomic proportions, while green chromic sulphate allows an excess of sulphuric acid to pass through the diaphragm. This result agrees with that of van Cleef, and indicates hydrolysis as the cause of the color-change.

3. With the help of the inversion of sugar it is shown that the extent and speed of the hydrolysis is dependent upon the temperature.

4. The acid formed by hydrolysis may be removed by successive shaking with a mixture of ether and alcohol, or by digestion with chromic hydroxide. This accelerates the hydrolysis.

5. Excess of acid accelerates the reversion to violet, and retards the formation of the green salt.

6. The formation of the green sulphate compound requires time, either from the double decomposition of the green chloride, or from hydrolytic action.

7. At 100°, a constant result is reached when the solution saturated with chromic hydroxide attains the atomic ratio $\text{Cr} : (\text{SO}_4)_2$; at 20°, the ratio is $\text{Cr}_5 : (\text{SO}_4)_4$.

8. The green substance occluded by baric sulphate from green chromic solutions also seems to be highly basic.

9. Migration experiments indicate no anion containing chromium in a green solution.

10. The molecular weight of one of the green substances is probably large.

11. All these experiments agree in pointing toward the existence of a green basic salt in which at least 47 per cent of the acid radical is replaced by hydroxyl. It is possible that there may be several compounds of different degrees of hydrolysis. The acid set free seems to be sulphuric acid, and not a complex acid. It is unsafe at present to apply any definite formula to the basic salt. Further investigation will be instituted in order to discover if possible its structure, as well as to determine whether or not a colloidal substance also exists in the hydrolyzed solution.

A CHRONOLOGICAL BIBLIOGRAPHY OF THE CHANGE IN CHROMIC SALTS FROM VIOLET TO GREEN.

BY FREDERIC BONNET, JR.

1828. Fischer, G.

Zur nähern Kenntniss der Chromsalze. Kastner's Archiv. f. Naturlehre, **14**, 164.

1838. Rose, H.

Ueber das Chlorchrom. Pogg. Ann., **45**, 183.

1841. Schrötter, A.

Ueber die Schwefelsäure-chromoxydsalze. Pogg. Ann., **53**, 513.

1842. Hertwig, C.

Ueber die in Wasser schwerlöslichen und unauf löslichen Modificationen des schwefelsäuren Kali-chromoxyd. Pogg. Ann., **56**, 95.

1843. Peligot, E.

Ueber das Chromsesquichlorür. C. R., **21**, 74-81.

1844. Kopp, E.

Note sur le sulfate chromique. C. R., **18**, 1156-58.

1844. Krüger.

Ueber die Farbenveränderung, welche das neutral Schwefelsäure-chromoxyd in der Auflösung in Wasser durch Erhitzen bis zum Kochpunkt erleidet. Pogg. Ann., **61**, 218.

1844. Berzelius, J. J.

Ueber die Allotropie einfacher Körper, als eine der Ursachen zur Isomerie ihrer Verbindungen. Pogg. Ann., **61**, 1.

1845. Loewel, H.

Ueber das Chromoxyd u. seine isomern Modificationen. Jl. de Pharm. et Chim. [3], 4 Ann., 321-344, 401-424; Centralbl., 1845, p. 561.

1845. Pelouze, J.

Note sur le sesquichlorure de chrome. Ann. de Chim. et Phys. [3], **14**, 247; Chem. Centralblatt, 1845, S. 603.

- 1847. Jacquelin.**
Etude de la réaction de l'acide sulfurique sur le bichromate de potasse; étude sur l'alun de chrom. C. R., **24**, 439.
- 1848. Traube, M.**
Ueber einige Chromverbindungen. Ann. der Chemie u. Pharm., **66**, 87.
- 1858. Fremy, E.**
Recherches sur les sels de chrome. C. R., **47**, 883.
- 1863. Siewert, M.**
Ueber die Farbenveränderung der Chromoxydsalzlösungen. Ann. der Chem. u. Pharm., **126**, 86.
- 1871. Heintze, L. J.**
Zur Kenntnis einiger Chromverbindungen. Jl. prak. Chemie N. F. [4], 211.
- 1872, 1873. Favre (P. A.) and Valson (C. A.)**
Recherches sur le dissociation cristalline. C. R., **74**, 1165; C. R., **77**, 577.
- 1874. Lecoq de Boisbaudran.**
Spectres lumineux, Paris, 1874, p. 186, planche xvi.
- 1874, 1875. Lecoq de Boisbaudran.**
Sur l'équilibre moléculaire des solutions d'alun de chrome. C. R., **74**, 1491 (1874); C. R., **80**, 764 (1875).
- 1875. Erhard, Th.**
Untersuchungen über die Absorption des Lichtes in einigen Chromsalzen. Inaug. Diss. 1875.
Also, Ueber den Unterschied zwischen den Absorptionsspectern der violetten u. grünen Lösungen der Chromoxydsalze.
- 1876. Wernicke, A.**
Ueber die Analogie des Chromoxyds mit den Oxyden der Ceritmetalle. Pogg. Ann., **159**, 575.
- 1877. Etard, A.**
Sur les sels de sesquioxyde de chrome. C. R., **84**, 1089.
- 1878. Vogel, H. W.**
Untersuchungen über Absorptionsspectra. Sitzungsberichte Berliner Akad., 1878, p. 409-431.
- 1880. Nelson (L. F.) and Petterson (O.)**
Ueber Molekularwärme und Molekularvolumina der seltenen Erden und deren Sulfate. Berichte, p. 1459.
- 1880. Bayley, Thos.**
On the Color Properties and Relations of Metals, — Cu, Ni, Co, Fe, Mn, and Cr. Jl. Chem. Society (London), **37**, 828.
- 1881. Doyer van Cleef, G.**
Ueber die Farbenveränderung der Chrom-oxydsalzlösungen. Jl. f. prak. Chem., **131**, 58.
- 1881. Doyer van Cleef, G.**
Ueber den Wasserverlust einiger Chromoxydsalze. Jl. f. prak. Chem., **131**, 69.

1882. Cross (C. F.) and Higgin (A.)

On the Reaction of Chromic Anhydride with Sulphuric Acid. *Jl. Chem. Soc. (London)*, **41**, 113.

1887. Recoura, A.

Recherches sur les chlorures de chrome. *Ann. de Chim. et Phys.*, 6^e serie, **10**, 5.

1890. Recoura, A.

Sur les états isomériques du sesquibromure de chrome. *C. R.*, **110**, 1029 et 1193.

1891. Knoblauch, O.

Absorptions Spektralanalysen sehr verdünnter Lösungen. *Ann. der Phys. u. Chem.*, **43**, 738.

1892. Marchetti, G.

Sul comportamento crioscopico delle soluzioni acquose del cloruro cromatico violetto e del cloruro cromatico verde. *Gaz. Chim. It.*, 22 II., 375-79; *Chem. Centralblatt*, 1892.

1892. Hartly, W. N.

On the Action of Heat on Solutions of the Salts of Chromium. *Chem. News*, **65**, 15.

1893. Klobb, T.

Contribution à l'étude des sels de sesquioxide de chrome. *Bull. Soc. Chim.* [3], **9**, 663-668.

1893. Lapraik, W.

Ueber die Absorptionspektren einiger Chromverbindungen. *Jl. prak. Chemie*, N. F. **47**, 305.

1893. Werner (A.) and Miolati (A.)

Beiträge zur Konstitution anorganischer Verbindungen. *Zt. phys. Chem.*, **12**, 35.

1893. Werner, A.

Beitrag zur Konstitution anorganischer Verbindungen. *Zt. anorg. Chem.*, **3**, 267; *Gaz. Chim. Ital.*, **27**, 1, 299-316.

1894. Recoura, A.

Sur les transformations moléculaires de quelques composés chromiques. *C. R.*, **118**, 1146.

1895. Piccini, A.

Ueber die Lösungen des grünen Chromchlorids $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. *Zt. anorg. Chem.*, **8**, 115. (*L'orosi* **17**, 329).

1895. Recoura, A.

Recherches sur le sulfate chromique ses transformations et les acides complexes qui en dérivent. *Ann. de Chim. et Phys.*, 7^e série, **4**, 494.

1895. Etard, A.

Sur l'origine moléculaire des bandes d'absorption des sels de cobalt et de chrome. *C. R.*, **120**, 1057.

1895. Recoura, A.
Sur les transformations moléculaire de l'hydrate chromique. C. R., 120, 1335.
1896. Patten, H. E.
Chromic Hydroxide in Precipitation. Am. Chem. Jl., 18, 608.
1896. Dougal, Margaret D.
Effect of Heat on Aqueous Solutions of Chrome Alum. London Chem. Soc. Transactions, 1526; Chemical News, 74, 278.
1896. Monti, V.
Ueber die Eigenthümlichkeiten der Chromalaun-lösungen. Zt. anorg. Chem., 12, 75 (abs.). Atti d. R. Acc. di Scienze (Torino); 30, 704.
1896. Whitney, W. R.
Untersuchungen über Chromsulfatverbindungen. Zt. phys. Chem., 20, 40.
1897. Long, J. H.
Jl. Am. Chem. Soc., 19, 683.
1897. Doyer van Cleef, G.
Maandbl. natuurw. 21, 34-41. A review of the work of Recoura in the previous ten years concerning the color change of Cr salts.
1897. Soret (Ch.), Borel (A.), and Dumont (E.).
Ueber die Brechungscoefficient der blauen u. grünen Lösungen des Chromalauns. Archiv. sc. phys. et nat. Genève (4), 3, 376-381. Zt. phys. Chem., 24, 170 (abs.).
1898. Venable (E. P.) and Miller (F. W.).
Nature of the Change from Violet to Green in Chrom Salt-solutions. Jl. Am. Chem. Soc., 20, 484; id. 22 (1900), 111.
1899. Recoura, A.
Sur l'acétate chromique. C. R., 129, 158.
1899. Recoura, A.
Sur les états isomérique de l'acétate chromique, acétate normal, acétate anormal, violet monoacide. C. R., 129, 208.
1899. Recoura, A.
Sur les états isomérique de l'acétate chromique, acétate anormal, violet biacide, acétate anormal, vert monoacide. C. R., 129, 288.
1899. Whitney, W. R.
Nature of the Change from Violet to Green in Chrom Salt-solutions. Jl. Am. Chem. Soc., 21, 1075.
1900. Pagel, C.
Sur un nouveau mode de production de sulfates doubles de chrome. C. R., 130, 1030.
1900. Richards (T. W.).
A note on Solid Solutions. Proc. Am. Acad., 35, 377; Zt. anorg. Chem., 23, 383.
1901. Werner (A.) and Gubser (M.).
Ueber die Hydrate des Chromchlorids. Berichte, 34, 1579-1604.

1901. Pfeiffer, P.

Ueber die Existenz des Trichlortriaquachroms. *Berichte*, **34**, 2559.

1901. Ferrero, Efsio.

Ueber die innere Reibung von Chromalaun-lösungen. *Zt. phys. Chem.*, **38**, 502 (abs.). *Nuovo Cimento* [5], **1**, 285-587, April, 1901.

1901. Férée, J.

Sur un nouvel hydrate de sesquioxide de chrome $\text{Cr}_2\text{O}_3\text{H}_2\text{O}$. *Bull. Soc. Chem.* [3], **25**, 620.

1901. Herz, W.

Zur Kenntnis einiger allotroper Modificationen von anorganischen Verbindungen. *Zt. anorg. Chem.*, **28**, 342.

1901. Koppel, J.

Alkoholhaltige Chromhalogenverbindungen. *Zt. anorg. Chem.*, **28**, 461.

1902. Wyruboff, G.

Recherches sur la constitution de composés de chrome. *Bull. Soc. Chim.*, Paris (3), **27**, 666-79; *Bull. Soc. Chim.*, Paris (3), **27**, 719-733; *Chem. Centralblatt*, 1902, Bd. 2, S. 423 u. 562.

